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A Polysiloxide Complex with two Chromium(III) η^2-Superoxo Moieties

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Abstract: The isolation and identification of intermediates formed in the course of the activation of dioxygen at transition metal centers reveals important mechanistic insights concerning such processes. We previously reported the reaction of the dinuclear Cr^{II} complex $[L_2Cr_2(MeCN)_2][Li(MeCN)]_2$ ($L = PhSi(OSiPh_2O^-)_3$) (**5**) with dioxygen, which resulted in the formation of the Cr^{IV} oxo complex $[L_2Cr_2O_2][Li(THF)_2]_2$ (**6**), as the final room temperature stable product. Here we now report the isolation and characterization of an intermediate en route to **6**, namely the dinuclear Cr^{III} superoxo complex $[L_2Cr_2(O_2)_2][Li(MeCN)]_2$ (**7**). **7** is the first example of a structurally characterized dinuclear Cr^{III} superoxo complex with two independent side-on bound superoxo ligands. Reactivity studies outline the capability of this superoxo complex to activate weak O–H bonds.

Keywords: Chromium · O–O activation · siloxide · superoxo

Insights into the mechanisms by which small molecules are activated, are of high value, as the latter, due to their ubiquity, are popular synthons in many industrial as well as biological processes. Like many other small molecules, dioxygen does not readily react with most organic molecules under ambient conditions due to high barriers for the primary reaction steps. This changes when O_2 is first activated through binding to transition metals such as iron, nickel, copper, chromium etc.[1] Binding often leads to electron transfer and thus to the formation of different dioxygen adduct complexes featuring superoxo ($O_2^{\bullet-}$) or peroxo (O_2^{2-}) ligands, bound either in an end-on or side-on fashion. From a subsequent reaction step metal hydroperoxo (HOO^-), oxo (O^{2-}) or hydroxo (HO^-) entities can result.[2] One synthetic system, which runs through several of such transformations in contact with O_2, was reported 2002 by Theopold and co-workers.[3] $[Tp^{tBu,Me}Cr(pzH')]BAr^F_4$ (**1**, pzH′ = 3-tert-butyl-5-methylpyrazole, BAr^F_4 = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) was reacted with dioxygen leading to the Cr^{III} superoxo complex $[Tp^{tBu,Me}Cr(pzH')(\eta^2\text{-}O_2)]BAr^F_4$ (**2**). In **2**, which represented the first structurally characterised Cr^{III} superoxo complex,[3,4] the superoxo ligand is bound side-on to the Cr^{III} center. **2** reacts further with one equivalent of **1**, thereby forming the Cr^{IV}=O complex **3**, which is capable of activating weak C–H bonds under formation of the Cr^{III} hydroxo complex **4** (Scheme 1).

We previously reported the reaction of the dinuclear Cr^{II} complex $[L_2Cr_2(MeCN)_2][Li(MeCN)]_2$ ($L = PhSi(OSiPh_2O^-)_3$) (**5**) with dioxygen in THF, which after work-up led to the isolation of the Cr^{IV} oxo complex $[L_2Cr_2O_2][Li(THF)_2]_2$ (**6**) (Scheme 2).[5] The primary dioxygen adduct had eluded characterisation, so that its identity remained unclear. As **5** possesses two chromium centers, different intermediates are conceivable to form in the initial oxygen activation step: Just one chromium center could react with one molecule of dioxygen, both chromium centers could cooperatively bind one dioxygen molecule or the two centers could react independently with two molecules of dioxygen. The investigations described below aimed on gaining insights concerning O_2 activation within this system. To gather information on the O_2 activation step, the reaction of dioxygen with **5** dissolved in THF was monitored UV/vis spectroscopically at room temperature. Thus the formation of a short-lived species could be observed, which decayed within minutes into the Cr^{IV} oxo complex **6** (345 nm and 453 nm).

As chromium dioxygen adducts are typically capable of reacting with weak C–H bonds, it is likely that the short lifetime of the intermediate is due to a reaction of this species with the solvent THF.[6] Therefore the UV/vis experiment was repeated in a solvent with stronger C–H bonds,[7] namely in DCM, at room temperature and at −20 °C. This gave rise to three absorption bands at 331, 543 and 875 nm; in addition a shoulder at 421 nm could be observed (Figure 1). These bands are located at similar positions compared to those observed for **2**, indicating the potential formation of a superoxo spezies with a side-on bound O_2 ligand. The species causing these absorptions proved to be more stable at temperatures below

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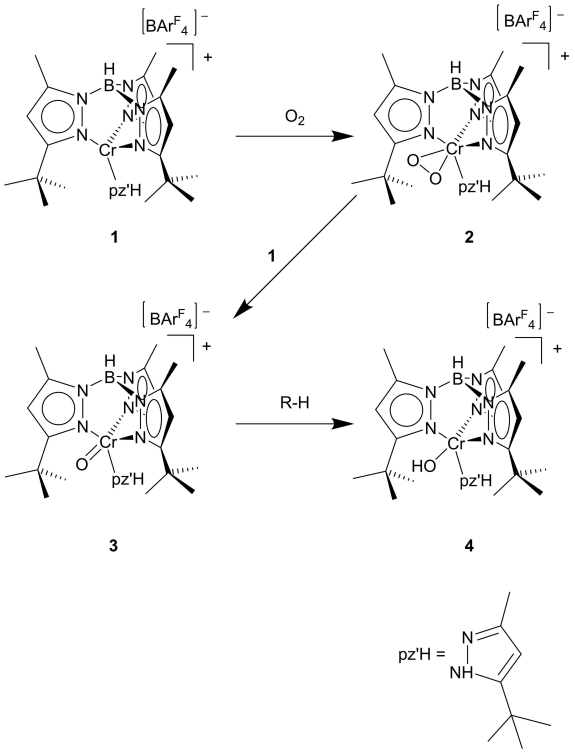
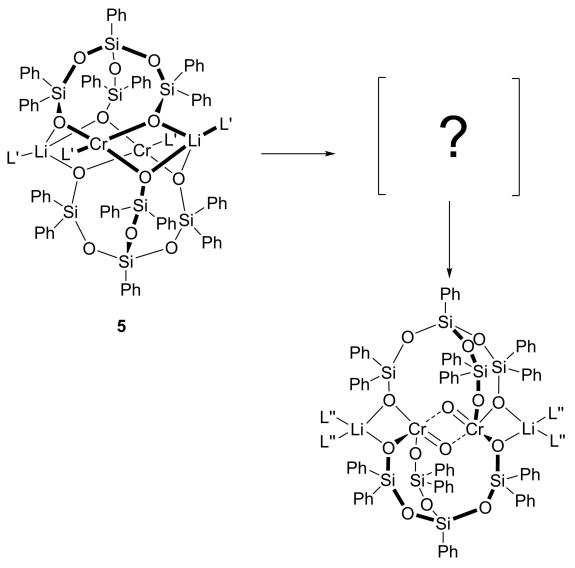


Scheme 1. Reaction of [Tp^{tBu,Me}Cr(pzH′)]BAr$^F_4$ (**1**) with dioxygen.



Scheme 2. Reaction of **5** with O_2 to give $[L_2Cr_2O_2][Li(L'')_2]_2$ L′ = MeCN, L″ = MeCN, THF (**6**).

−20 °C than the intermediate formed under the same conditions in THF. Still, the decay of the absorption bands of the intermediate and the formation of bands typical for **6** dissolved in DCM could be observed at temperatures above −20 °C. To determine what kind of dioxygen adduct had been formed during this initial activation step at low temperatures,

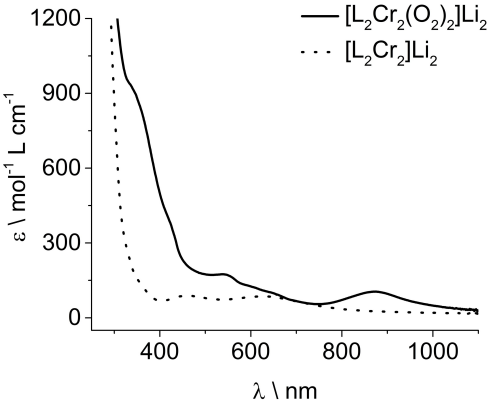


Figure 1. UV/Vis absorption spectrum of **5** (0.7 mmol in DCM, dashed line) and the spectral changes upon addition of O_2 at −20 °C.

attempts to grow single crystals of the product at −80 °C in DCM as well as THF were undertaken. While these failed for THF, the increased stability in DCM allowed for the growth of temperature- and moisture-sensitive single crystals of the product through layering a saturated solution with hexane at −80 °C. X-ray analysis led to the structure of $[L_2Cr_2(O_2)_2][Li(MeCN)]_2$ (**7**) revealing that each chromium center is binding one O_2 molecule in a side-on fashion (Figure 2). The O–O bond distance of 1.346(9) Å is in good agreement with values previously observed for chromium siloxide complexes with end-on bound superoxo ligands (1.334(7), 1.324(7) and 1.334(4) Å).[5,8]

The assignment as a superoxo ligand was corroborated by Resonance Raman measurements: After bubbling $^{16}O_2$ into a DCM solution of **5** a new band at 1100 cm^{-1} appeared, which was shifted to 1049 cm^{-1} when $^{18}O_2$ was employed. Both the position of the bands and the isotopic shift of $\Delta(^{16}O–^{18}O)$ = 51 cm^{-1} are typical for chromium bound superoxo ligands (Figure 3).[4a,5,8–9] From these results it can be concluded that

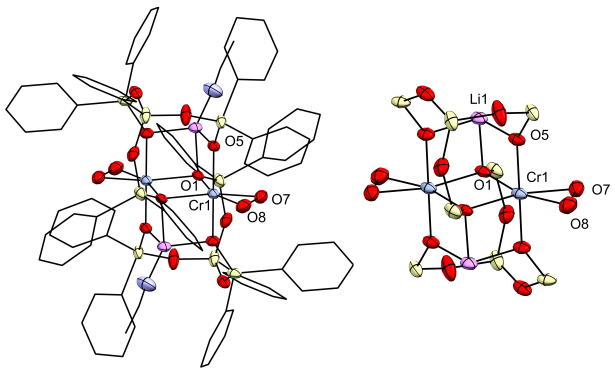


Figure 2. Left: Molecular structure of **7**. Right: Core of **7**. For clarity hydrogen atoms are omitted. Selected bond length in [Å] Cr1–O7 1.921(6), Cr1–O8 1.955(7), O7–O8 1.346(9).

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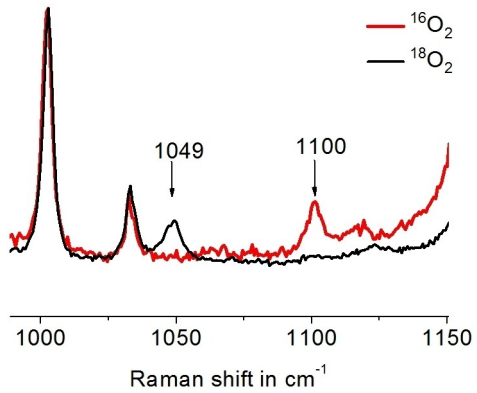


Figure 3. Resonance Raman spectra of **7** recorded after treating **5** with $^{16}O_2$ (red line) and with $^{18}O_2$ (black line) in dichloromethane at −50 °C, excitation wavelength 488 nm.

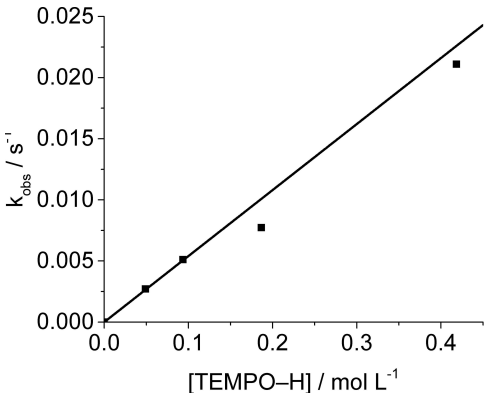


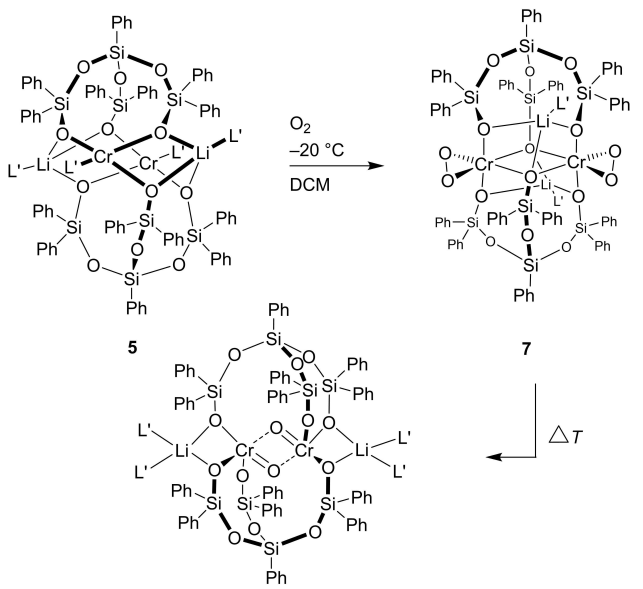
Figure 4. Plot of pseudo first-order rate constant (k_{obs}) versus the concentration of TEMPO-H to determine the second order rate constant.

the reaction of **5** with dioxygen involves the formation of the dinuclear Cr^{III} superoxo complex **7** as an intermediate (Scheme 3). The formation of such a complex is very uncommon, as typically upon activation of the first O_2 molecule at one metal center of a dinuclear complex the superoxo entity thus formed immediately reacts/interacts with the second metal center in close proximity. This makes **7** to our knowledge the only precedent case of a structurally characterized dinuclear complex with two isolated superoxo sites formed in course of an O_2 activation reaction.

As Cr^{III} superoxo complexes are known to activate weak O–H bonds,[4c,8,10] we employed TEMPO-H as a substrate to test the reactivity of **7**. The reaction mixture was analyzed by means of EPR spectroscopy, which revealed the formation of a nitroxide radical confirming that **7** is capable of abstracting a hydrogen atom from TEMPO-H (Figure S1). The reaction was also monitored UV/vis spectroscopically and subsequently pseudo-first order rate constants were determined (Figure S2). These increased linearly with an increase in the concentration of TEMPO-H and gave a second order rate constant of $5.4 \pm 0.2 \cdot 10^{-2}\ M^{-1}s^{-1}$ for complex **7** in DCM at −20 °C (Figure 4). Since this is the first example of a reactivity study performed on a dinuclear Cr^{III} superoxo complex, the second order rate constant of **7** can only be compared to the rate constant determined for mononuclear Cr^{III} superoxo complexes and then it is reasonable to focus on siloxide-based ligand systems. Hence, $[L'''_2Cr\text{-}\eta^1\text{-}O_2]Li_2(THF)_4$ ($L''' = {}^{-}OSiPh_2OSiPh_2O^{-}$) (**8**), which has an *end-on* bound superoxo ligand, is a well suited candidate and the comparison showed, that **7** is much less reactive than the mononuclear complex **8** ($k_2 = 160 \pm 1 \cdot 10^{-2}\ M^{-1}s^{-1}$, −80 °C in THF).

This is in agreement with systems described in literature, where mononuclear copper complexes with side-on bound superoxo ligands were found to display a much lower hydrogen atom abstraction reactivity than their corresponding end-on bound variants.[11]

In conclusion we have been able to show that the dinuclear Cr^{IV} oxo complex formed in the reaction of the Cr^{II} complex $[L_2Cr_2(MeCN)_2][Li(MeCN)]_2$ (**5**) with dioxygen at room temperature is preceded by an intermediate that features two Cr^{III} superoxo moieties. The latter could be crystallized and spectroscopically characterized after lowering the reaction temperature and using a solvent with stronger C–H bonds. This compound represents the first structurally characterized dinuclear complex, in which both metal centers activate dioxygen independently. The superoxo ligands are bound in a side-on fashion to the chromium centers and are capable of reacting with weak O–H bonds.



Scheme 3. Synthesis of **7** with L′ = MeCN.

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Conflict of Interest

The authors declare no conflict of interest.

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